Freezing Point Depression of Aqueous Solutions of DEEA, MAPA and DEEA-MAPA with and without CO2 Loading

Waseem Arshad, Muhammad; Thomsen, Kaj

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Freezing Point Depression of Aqueous Solutions of DEEA, MAPA and DEEA-MAPA with and without CO_2 Loading

Muhammad Waseem Arshad

Supervisor: Assoc. Prof. Kaj Thomsen

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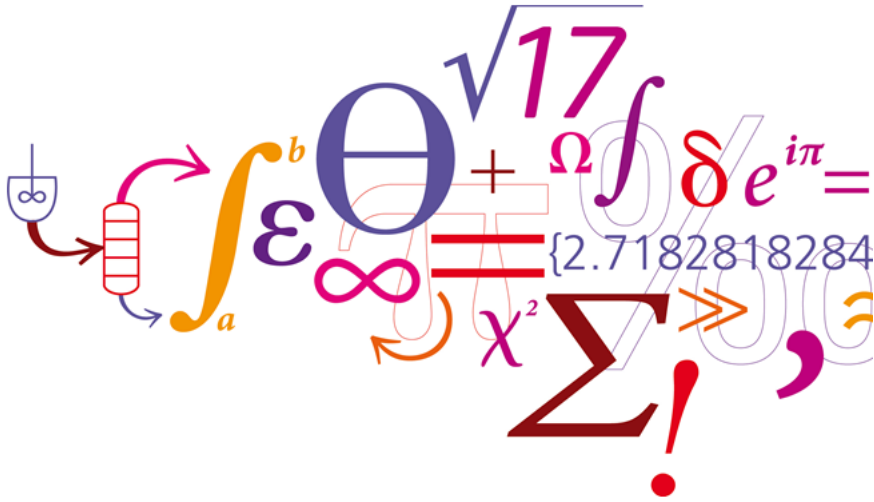


DTU Chemical Engineering
Department of Chemical and Biochemical Engineering

PRESENTATION OUTLINE

- Introduction
- Materials
- Reaction Mechanism
- Experimental Method
- Results
- Conclusions
- Future Work

INTRODUCTION

Freezing Point Depression:

The phenomenon in which the freezing point of a Liquid (Solvent) is depressed when another compound is added in it. This means that the solution has lower freezing than the pure solvent.

Why we need Freezing Point Depression Data???

- We want to model H_2O-DEEA-MAPA-CO_2 system
- Water activity is a key parameter for the amount of water evaporated in the desorber
- Low water activity means less evaporation of water in the desorber and low energy consumption during solvent regeneration
- Water activity can be determined very accurately from Freezing point data

MATERIALS

- **2-(Diethylamino)-ethanol OR DEEA (99%)**

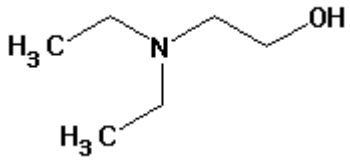
  Clear liquid with light yellow colour

  Freezing point = -70 ^{o}C

  Boiling point = 163 ^{o}C

  pH = 11.5 at 100 g/l at 20 ^{o}C

  Completely soluble in water



- **3-(Methylamino)propylamine OR MAPA (97-98%)**

  Clear and colourless liquid

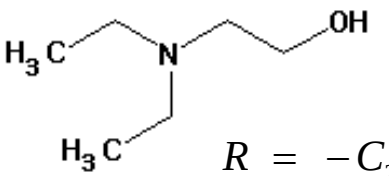
  Freezing point = -72 ^{o}C

  Boiling point = 140 ^{o}C

  pH = 13.5 at 100 g/l at 20 ^{o}C

  Completely soluble in water

REACTION MECHANISM



2-(Diethylamino)-ethanol OR DEEA

$$R = -C_2H_5$$
$$R' = -CH_2CH_2OH$$
$$\therefore \quad \text{DEEA} = R_2R'N$$

Base catalytic effect on hydration of CO_2

$$R_2R'N + H_2O + CO_2 \rightarrow R_2R'N^+H + HCO_3^- \qquad (1)$$

Zwitterion mechanism

$$R_2R'N + CO_2 \leftrightarrow R_2R'NCOO^- \qquad (1a)$$

$$R_2R'NCOO^- + H_2O \rightarrow R_2R'N^+H + HCO_3^- \qquad (1b)$$

Following reactions may also take place simultaneously

$$CO_2 + OH^- \leftrightarrow HCO_3^- \qquad (2)$$

$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \qquad (3)$$

[Ref] Vaidya, P. D.; Kenig, E. Y. A Study on CO2 Absorption Kinetics by Aqueous Solutions of *N*,*N*-Diethylethanolamine and *N*-Ethylethanolamine. *Chem. Eng. Technol.* **2009**, *32*, No. 4, 556-563

REACTION MECHANISM

3-(Methylamino)propylamine OR MAPA

$R = -C_3H_6$ and $R' = -CH_3$

$\therefore$ MAPA $= H_2NRR'NH$

Protonation:

$$H_2NRR'NH + H^+ \leftrightarrow H_2NRR'NH_2^+ \quad (1)$$

$$H_2NRR'NH + H^+ \leftrightarrow {}^+H_3NRR'NH \quad (2)$$

$$H_2NRR'NH + 2H^+ \leftrightarrow {}^+H_3NRR'NH_2^+ \quad (3)$$

8 Possible species of MAPA

Carbamate:

$$H_2NRR'NH + CO_2 \leftrightarrow H_2NRR'NCOO^- + H^+ \quad (4)$$

$$H_2NRR'NH + CO_2 \leftrightarrow {}^-OOCHNRR'NH + H^+ \quad (5)$$

$$H_2NRR'NH + 2CO_2 \leftrightarrow {}^-OOCHNRR'NCOO^- + 2H^+ \quad (6)$$

Protonated Carbamate:

$$H_2NRR'NCOO^- + H^+ \leftrightarrow {}^+H_3NRR'NCOO^- \quad (7)$$

$${}^-OOCHNRR'NH + H^+ \leftrightarrow {}^-OOCHNRR'NH_2^+ \quad (8)$$

EXPERIMENTAL METHOD

A, Thermostatic bath with ethanol

B, Cooling jacket

C, Sample glass with magnetic stirrer

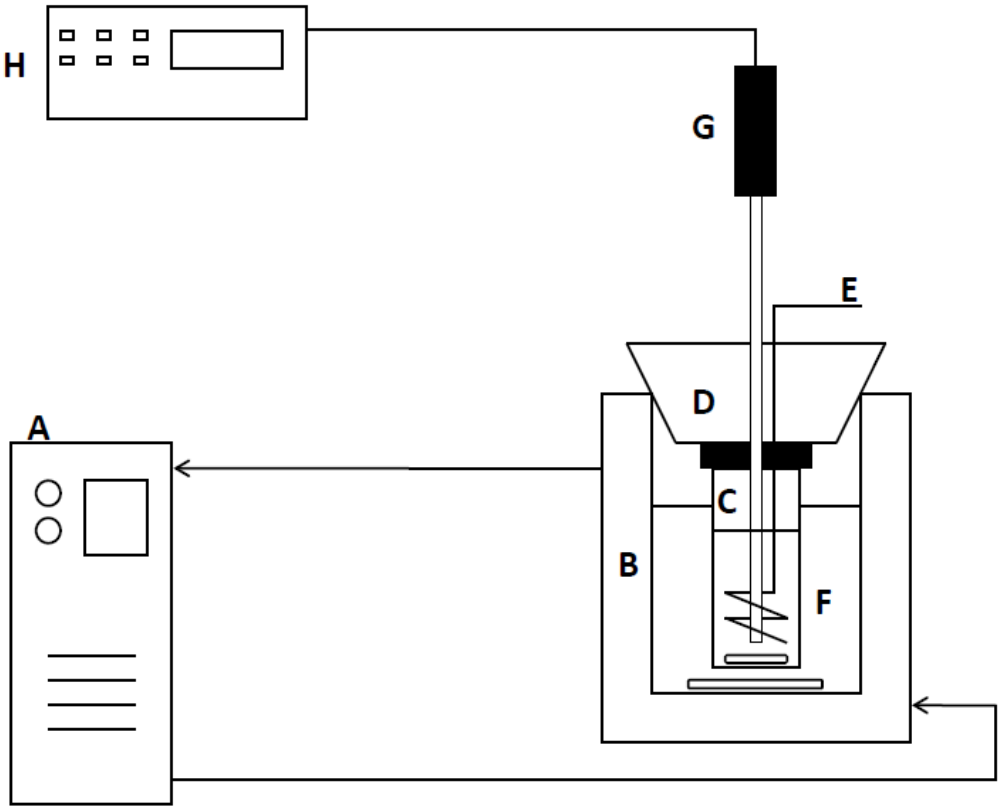
D, Rubber stopper with sample glass lid

E, Device for manual stirring

F, Controlled temperature ethanol bath with magnetic stirrer

G, Pt100 Thermometer

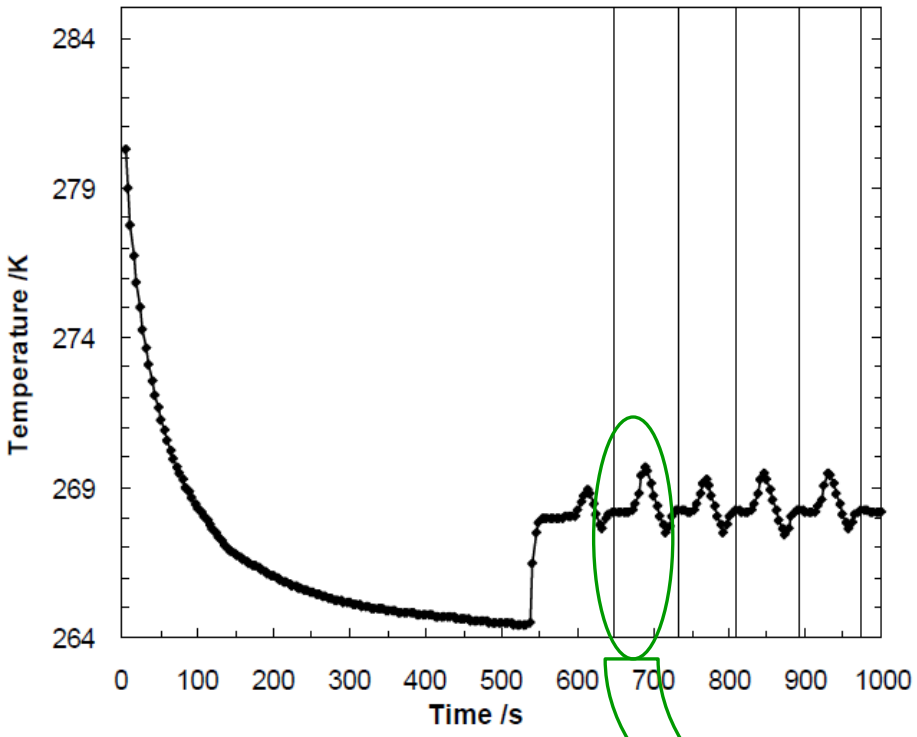
H, Data acquisition unit

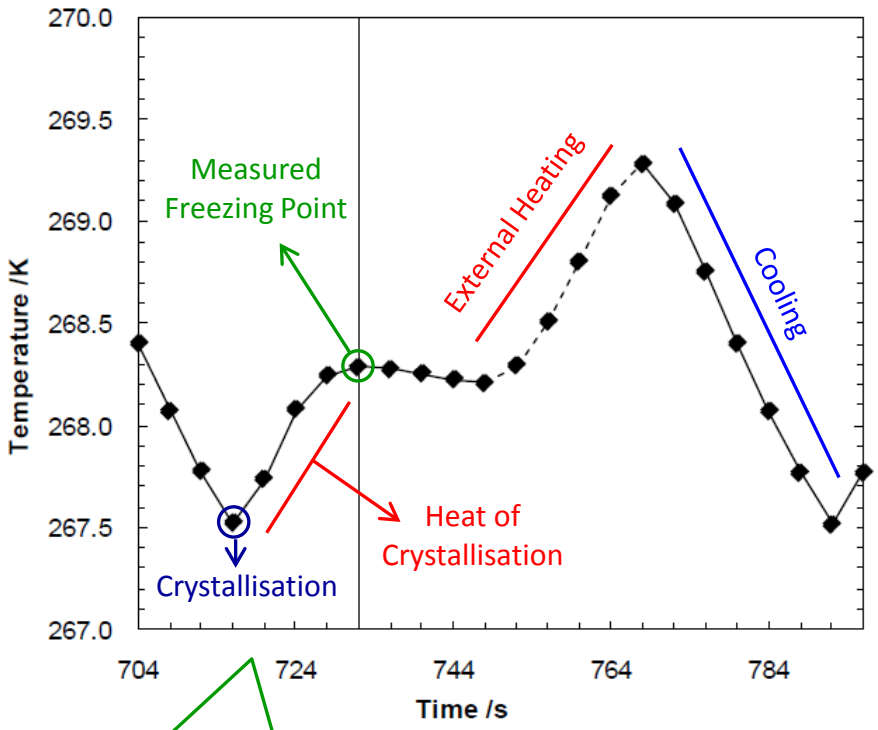


Experimental Setup

[Ref] Fosbøl, P. L.; Pedersen, M. G.; Thomsen, K. Freezing Point Depressions of Aqueous MEA, MDEA, and MEA-MDEA Measured with a New Apparatus. *J. Chem. & Eng. Data* **2010**, Special Issue: John M. Prausnitz Festschrift

EXPERIMENTAL METHOD





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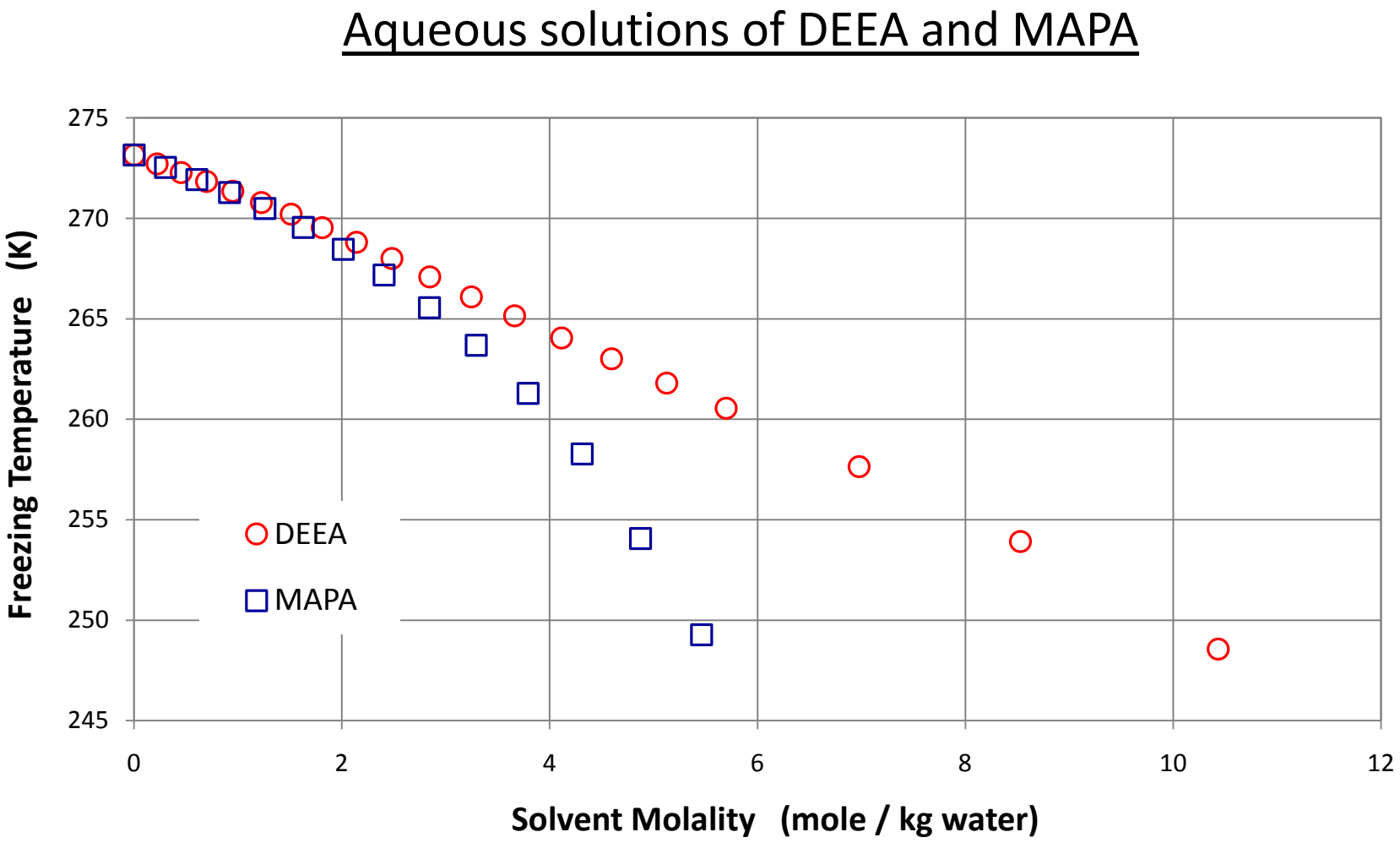
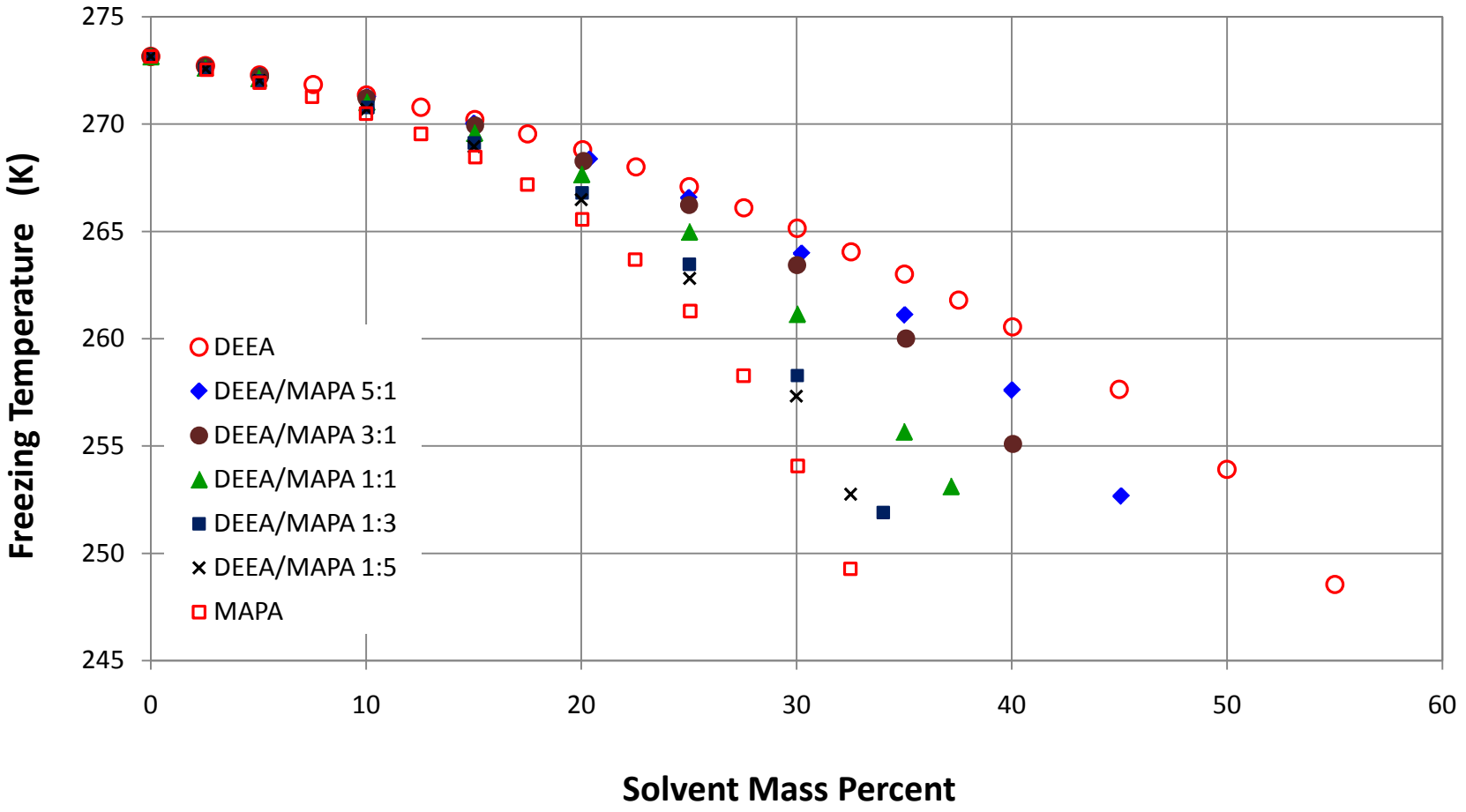
RESULTS


Aqueous solutions of DEEA and MAPA
Freezing Temperature (K)
275
270
265
260
255
250
245
0
2
4
6
8
10
12
DEEA
MAPA
Solvent Molality (mole / kg water)

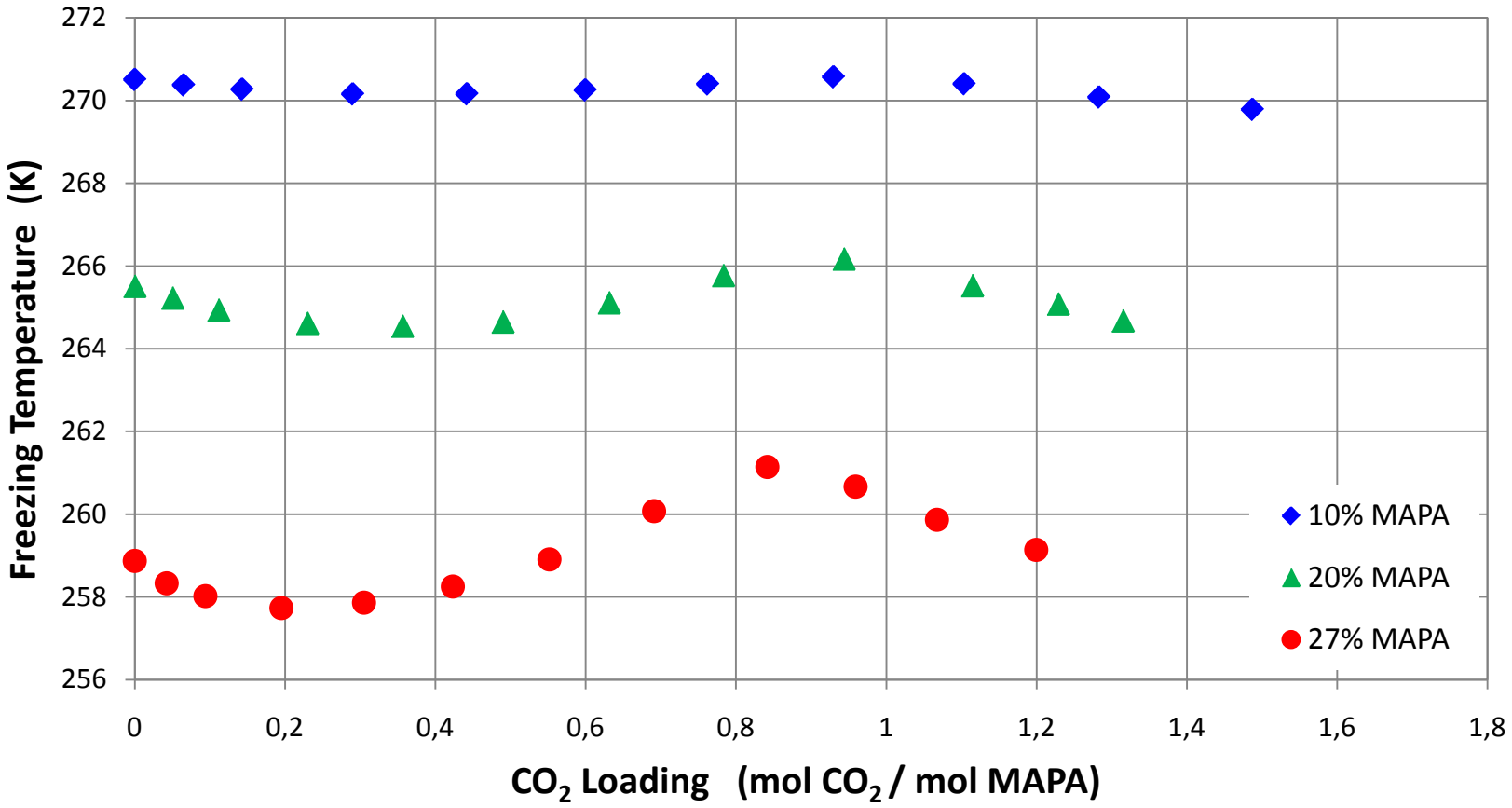
RESULTS

Aqueous solutions of DEEA-MAPA with different molar ratios



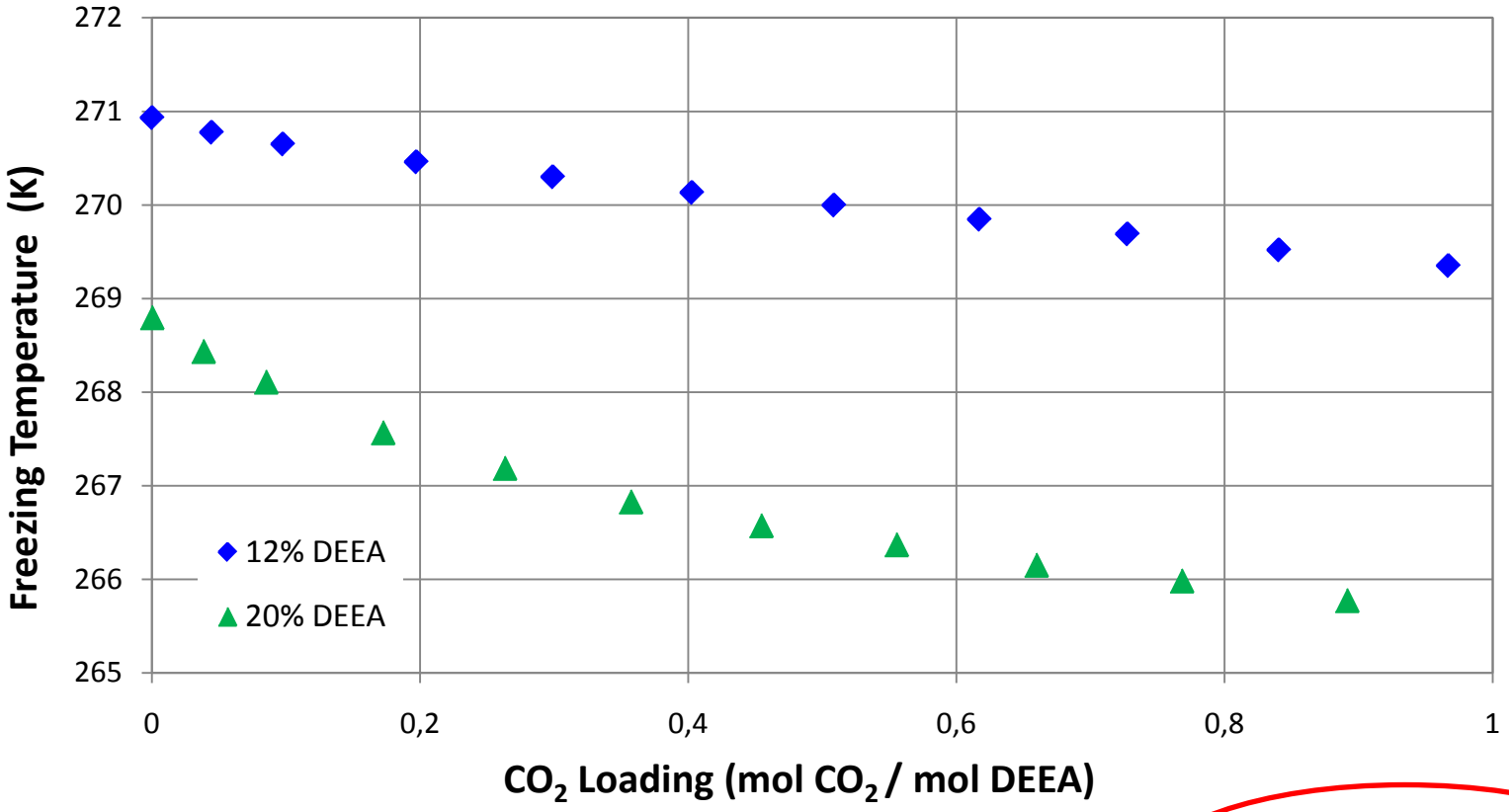
RESULTS

Aqueous solutions of MAPA loaded with CO_2



RESULTS

Aqueous solutions of DEEA loaded with CO_2



Work in Progress for 30% and 35% DEEA solutions

CONCLUSIONS

- Freezing point depression (FPD) are measured for H_2O-DEEA and H_2O-MAPA and also for H_2O-DEEA-MAPA for different molar ratios of DEEA/MAPA [Data point = 76]

- FPD are measured for H_2O-DEEA-CO_2 and H_2O-MAPA-CO_2 systems at different CO_2 loading [Data points = 57]

- Measured freezing point data illustrates that the MAPA-water interaction is stronger than DEEA-water interaction

- The measured data can be used for modeling CO_2 absorption/ desorption system when aqueous blend of DEEA/MAPA is used

FUTURE WORK

- Measurement of FPD for 30% and 35% DEEA solutions with different CO_2 loadings
- Measurement of freezing points For aqueous solutions of DEEA-MAPA with different molar ratios loaded with CO_2
- Development of correlations for the freezing points as a function of the solution composition
- Thermodynamic modeling of H_2O-DEEA-MAPA-CO_2 system using Extended UNIQUAC model

THANK YOU
FOR
YOUR ATTENTION

QUESTIONS ?????